

Electronic Structure and Volatility of Group-8 Oxides MO₄, where M = Ru, Os, and Element 108, Hs

V. Pershina,^{1,3} T. Bastug,² B. Fricke,² S. Varga³

¹GSI, Darmstadt; ²Universität Kassel, Kassel;

³Institut für Kernchemie, Universität Mainz, Mainz

The discovery [1] of a relatively long-lived isotope of element 108, Hs, makes it now possible to design chemical experiments studying its chemical properties. Hs is expected to be a member of group 8 of the Periodic Table and, thus, a homolog of Ru and Os. If the chemical properties of Hs are comparable to those of Ru and Os, it should form a very volatile tetroxide, HsO₄. Several experimental groups including one from Mainz/GSI are, therefore, preparing gas-phase experiments on studying volatility of OsO₄ and its homologs, RuO₄ and OsO₄.

In the current report, we present results of the fully relativistic electronic structure calculations for group 8 gas-phase tetroxides, RuO₄, OsO₄, and HsO₄, and predict their volatility as an adsorption enthalpy with respect to the particular experimental conditions. The electronic structure calculations of MO₄ (M = Ru, Os, and Hs) including the geometry optimization were performed using the fully relativistic *ab initio* Density-Functional method in the GGA approximation for the exchange-correlation potential [2]. The calculated bond lengths, bond strengths, effective charges and covalence effects (OP) of these molecules are shown in Table 1. They indicate that HsO₄ is the most stable and the most covalent compound in the row.

The adsorption enthalpy of MO₄ on the quartz surface of the chromatography column was calculated using the following model of a molecule-slab interaction

$$E(x)_{\text{molecule-slab}} = -(\pi/6)NC_1/x^3, \quad (1)$$

where N is the number of atoms per cm³ and x is the molecule-surface interaction distance. In the case of the dispersion interaction of a polarizable molecule with an inert surface consisting of molecular units

$$C_1 = \frac{3}{2} \frac{\alpha_1 \alpha_2}{\left(\frac{1}{hv_1} + \frac{1}{hv_2} \right)} \quad (2)$$

where hv_1 and hv_2 denote roughly ionization energies, and α_1 and α_2 - polarizabilities of the molecule (1) and the surface (2), respectively. Using the relation between polarizability of the surface and its dielectric constant, eqs. (1) and (2) transform into

$$E(x) = -\frac{3}{16} \left(\frac{\varepsilon - 1}{\varepsilon + 2} \right) \frac{\alpha_{mol}}{\left(\frac{1}{hv_{slab}} + \frac{1}{hv_{mol}} \right)} x^3 \quad (3)$$

where $\varepsilon = 3.81$ is taken for the highest quartz modification - glass.

Table 1. Calculated bond lengths R_e (in Å), bond strengths D_e (in eV), ionization potentials IP (in eV), polarizabilities α (in a.u.), effective charges Q_M and overlap populations (OP) of MO₄ (M = Ru, Os, and Hs)

Property	RuO ₄	OsO ₄	HsO ₄
R_e (calc.)	1.73	1.75	1.81
R_e (exp.) [3]	1.706	1.711	-
D_e (calc.)	27.48	27.71	28.44
α (calc.)	43.73	40.22	42.24
IP (calc.)	12.25	12.35	12.28
IP (exp.) [4]	12.19	12.35	-
Q_M	1.45	1.46	1.39
OP	1.92	1.94	2.17

By putting the experimental, when available, or calculated parameters into eq. (3), interaction energies $E(x)$ were calculated as shown in Table 2. In the case when the SiO₂ surface is covered with adsorbed O₂, or has an effective charge ($Q=-0.4$), models similar to that of eqs. (1-3) were used giving the interaction energies listed in Table 2 as well.

Table 2. Contributions to the interaction energies $E(x)$ between the neutral MO₄ (M = Ru, Os, and Hs) molecules and a) pure quartz surface; b) surface covered with O₂; c) surface with effective charge Q_e ($Q = -0.4$)

Molecule	α - $\alpha(\text{SiO}_2)$ $E10^{24} x^3$ (eV cm ³)	α - $\alpha(\text{O}_2)$ $E10^{24} x^3$ (eV cm ³)	α - Q_e $E10^{32} x^4$ (eV cm ⁴)
RuO ₄	4.73	6.28	10.01
OsO ₄	4.48	6.01	9.41
HsO ₄	4.64	6.16	9.73

The unknown distance x (of 2.25 Å for OsO₄ in the case “a”) was deduced from the experimental $\Delta H_{\text{ads}}(\text{OsO}_4)$ by setting $E(x)$ equal to -38 ± 1.5 kJ/mol. Taking $x=2.25$ Å as a benchmark and assuming that the molecule-surface distance is directly related to the size of the interacting molecules, the adsorption enthalpies for RuO₄ and HsO₄ were calculated using the data of Table 2. The obtained ΔH_{ads} for RuO₄ and HsO₄ (independently of the model) are larger and smaller than $\Delta H_{\text{ads}}(\text{OsO}_4)$ by about 2 kJ/mol, respectively. Thus, the volatility has the trend RuO₄ < OsO₄ < HsO₄, with the differences between the species being almost within the experimental uncertainties.

References

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